EFFECTS OF WATER HARDNESS ON SPRAY DROPLET SIZE UNDER AERIAL APPLICATION CONDITIONS

W. C. Hoffmann, W. E. Bagley, B. K. Fritz, Y. Lan, D. E. Martin

ABSTRACT. *Minerals and organic matter in spray carrier water can reduce the effectiveness of some plant protection products. Water hardness has been found to have a significant impact of the efficacy of some crop protection materials and has shown conflicting influence on spray droplet size. The objectives of this study were to determine the effects of water hardness on spray droplet size produced by two commonly-used aerial spray nozzles with and without the addition of an invert suspension adjuvant to the tank solution under aerial application conditions.*

Water hardness levels from 0 to 800 ppm and/or the addition of a spray adjuvant to a spray solution had a significant effect on spray droplet size. The spray adjuvant, an invert suspension, increased most spray droplet size parameters and decreased the percent of spray volume contained in droplets less than 200 µm as long as the water hardness did not exceed 200 ppm. The spray adjuvant had little effect on relative span when the spray was released at a 45° angle to the high speed airstream, but lowered the relative span for sprays orientated 0° or straight back relative to the high speed airstream. Aerial applicators should test the water used in making tank solution for water hardness before the addition of spray adjuvants.

Keywords. *Aerial application, Water hardness, Spray adjuvant, Droplet size, Adjuvant.*

The atomization process of converting liquid into spray droplets depends on physical properties of the formulation, spray volume, nozzle type, working pressure, and ambient conditions at the time of application. Minerals and organic matter in spray carrier water can reduce the effectiveness of some plant protection products. This antagonism is related to the salt concentration from various elements such as calcium and magnesium, which also cause water hardness. Ratajkiewicz and Kierzek (2004) investigated the influence of water hardness on the droplet size spectrum from liquid containing fungicides in different formulation related to ground sprayer applications. The authors found that droplet sizes expressed as volume median diameter ($D_{V0.5}$) or other diameters were not significantly affected by water hardness in the range from distillate (0 ppm) to 685.8-ppm $CaCO_3$. Water hardness irregularly influenced droplet size produced by a flat fan nozzle. It was shown that an increase of calcium and magnesium ions in spray solution increases the droplet size.

Klokocar-Smit et al. (2002) found that the physical and biological compatibility of plant protection products applied in short succession or in tank mix depends on active materials, formulation, and quality of water for spray preparation. The well water used in the study differed in quality by higher pH, hardness, and content of NO_2^-, Fe^{2+}, Fe^{3+}, NH_4^+, Ca^{2+}, and organic materials in comparison to drinking tap water. These ions affected the physical traits of spray liquids, the ability to tank mix with multiple compounds, and the quality of vegetable protection. The pH of fungicide tank mixed with insecticide suspensions was higher in raw water compared to tap water. Stability of mixtures decreased in tank mix of Pyrinex 48-EC or Sucip 20-EC with either Mankogal-80 or Folpan WP-50, and surface tension decreased, when pure water was used. A possible interaction might exist between tank mix fungicide, insecticide, and water mineral content, which influenced its efficacy against *Alternaria alternata* spore germination and Colorado potato beetle mortality. Some tank mixes were phytotoxic on tomatoes. The low quality of tap water restricted the choice of tank mix combinations.

Some surfactant and other activator adjuvants for herbicides increase herbicide activity and encompass a wide variety of surfactants. Many researchers have studied the modes of activator action including reduction of spray solution surface tension to enhance contact area, solubilization of the leaf cuticle, emulsifier action, increased spray retention, protection of the herbicide in the spray solution, promotion of rainfastness, acting as a cosolvent or copenetrant, modification of spray deposition on plant foliage, and enhanced movement on the foliage surface to areas of greater absorption (Price, 1982; Wills and McWhorter, 1985; Penner et al., 1999; Roggenbuck et al., 1990, 1994; Wade et al., 1993; Thelen et al., 1995).

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Objectives

The objectives of the present study were:

- to determine the effects of water hardness on spray droplet size produced by two commonly used spray nozzles;
- to determine the effects and interactions between water hardness and an invert suspension spray adjuvant on spray droplet size.

Methods

This study was comprised of two treatments, each a different nozzle configuration that was chosen to represent common operational conditions used by aerial applicators. Each treatment was conducted over 10 spray formulations that consisted of five levels of water hardness, one active ingredient, and one adjuvant. The active ingredient was used at the same rate in all formulations. Each water hardness level was test both with and without the adjuvant. Each treatment and spray formulation combination was replicated sequentially three times. The specific testing protocol, nozzle configurations, spray formulations, and physical property measurements are discussed below.

Spray Formulations

Atomization test treatments consisted of a CP11TT 8008 flat fan nozzle (CP Products Inc., Mesa, Ariz.) operated at two configurations; 45° orientation at 207 kPa (30 psi) (Treatment 1), and 0° orientation at 414 kPa (60 psi) (Treatment 2). For each treatment, five levels of water hardness, both with and without an adjuvant (invert suspension added at a rate of 15 g per L (4 oz. per 20 gal), Wilbur-Ellis Co., San Antonio, Tex.) added to the tank solution, were examined. CaCl was added to distilled water to obtain the water hardness levels. Kocide® 4.5LF (EPA No. 352-684, DuPont, Wilmington, Del.) was included in each tank mix as the active ingredient. Table 1 shows tank mixes for each water hardness level. All tests were conducted in a 60-m/s (125-mph) airstream.

Droplet Sizing System

A Sympatec Helos laser diffraction droplet sizing system (Sympatec Inc., Clausthal, Germany) was used to measure droplet size data. The Helos system uses a 623 nm He-Ne laser and was fitted with an R5 lens, which resulted in a dynamic size range of 0.5 to 875 μm in 32 sizing bins. The Sympatec traversed vertically through the spray plume using a forklift mounted frame. Each replication consisted of a 15-s vertical traverse of the total spray cloud by the laser diffraction system at a distance of 61 cm (24 in.) from the nozzle. Tests were performed within the guidelines provided by ASTM Standard E1260: Standard Test Method for Determining Liquid Drop Size Characteristics in a Spray Using Optical Nonimaging Light-Scattering Instruments (ASTM, 2003).

Table 1. Spray formulations for water hardness levels.

Hardness (ppm)	Tank, L (gal)	Kocide, kg (lb)	CaCl (g)
0	113.5 (30)	1.4 (3)	0.0
100	113.5 (30)	1.4 (3)	41.7
200	113.5 (30)	1.4 (3)	83.5
400	113.5 (30)	1.4 (3)	166.9
800	113.5 (30)	1.4 (3)	333.8

Droplet sizing data measured included volume median diameter ($D_{V0.5}$), the 10% and 90% diameters ($D_{V0.1}$ and $D_{V0.9}$), the relative span (RS), and the percent volume less the 100 μm (ASTM E1620 (2004). $D_{V0.5}$ is the droplet diameter (μm) where 50% of the spray volume or mass is contained in droplet of lesser diameter. $D_{V0.1}$ and $D_{V0.9}$ values describe the proportion of the spray volume (10% and 90%, respectively) contained in droplets of the specified size or less. The percent volume less than 100 μm was included as an indicator of the "driftable" portion of a spray. The Relative Span (RS) (eq. 1) is a dimensionless measure of the spread of the droplet sizes in the spray.

$$RS = \frac{D_{V0.9} - D_{V0.1}}{D_{V0.5}} \tag{1}$$

Statistical Analyses

The statistical analyses used the SAS Mixed Model procedure (Littell et al., 1996) to test the effects of the water hardness with and without a spray adjuvant on spray droplet size parameters. Statistical significance between means was specified at the 0.05 level of significance and separated by Duncan's mean separation.

Results

The two configurations of the CP11TT 8008 flat fan nozzle were selected to represent two different application scenarios. Treatment 1 [45° orientation at 207 kPa (30 psi)] represented a situation where the spray liquid experiences significant stress on the liquid spray as it encountered the high speed airstream at a 45° angle. Treatment 2 [0°orientation at 414 kPa (60 psi)] resulted in much less stress on the fluid as a result of the liquid being emitted parallel to the airstream resulting in the spray liquid having a lower velocity relative to the airstream. Bouse et al. (1994) provided a more complete description of this principle.

Statistical Analyses for Droplet Size Parameters

The two treatments were highly significantly different ($p < 0.0001$, df = 58). Therefore, the effects of water hardness and spray adjuvant were independently analyzed for each treatment. In the statistical analyses of the fixed effects in each treatment (water hardness (WH) and the spray adjuvant) (table 2), water hardness had a significant or a highly significant effect on droplet size parameter for both treatments. The differences in droplet size due to the presence or absence of a spray adjuvant in the tank solution were not as conclusive since the statistical significance ranged from highly significant to non-significant for different combination of droplet size parameters and treatment in no consistent pattern. The interaction between water hardness and spray adjuvant was highly significant for all combinations of treatment and droplet size parameters, except for Relative Span in Treatment 1; therefore, further exploration of this interaction was warranted. The analyses are presented by Treatment for clarification.

Treatment 1 Analyses

A visual assessment (fig. 1) of the droplet size parameters indicates many of the trends that are supported by the statistical analyses (table 3). The data in figure 1 are

Table 2. Statistical analyses of the fixed effects by treatment.

	df[a]	$D_{V0.1}$[b]	$D_{V0.5}$[b]	$D_{V0.9}$[b]	Relative Span	%Vol <100μm
Treatment 1						
Hardness	4	*	*	**	**	*
Adjuvant	1	*	ns	*	ns	*
Hardness*Adjuvant	4	**	**	**	ns	**
Error	21					
Treatment 2						
Hardness	4	**	**	**	*	**
Adjuvant	1	**	ns	*	**	**
Hardness*Adjuvant	4	**	**	**	**	**
Error	23					

[a] df = degrees of freedom in statistical analyses.
[b] * - statistical significance (P < 0.05); ** - highly statistical significant (P < 0.01); ns - not statistical significant.

presented as paired data (with or without a spray adjuvant in the tank solution) for three droplet size parameters ($D_{V0.1}$, $D_{V0.5}$, and $D_{V0.9}$) by water hardness level. Generally, increased water hardness resulted in larger spray droplets (fig 1). For water hardness levels from 0 to 200 ppm, the addition of the adjuvant increased the droplet size of the $D_{V0.1}$, $D_{V0.5}$, and $D_{V0.9}$ measurement; however, this increase was only statistically significant at the 100-ppm level (table 3).

Treatment 1 created a high shear stress on the spray liquid as the liquid encounters the high speed air at a 45° angle. The spray adjuvant reduced the amount of small particles that were created during the atomization process. For water hardness levels at 400 and 800 ppm, the addition of the adjuvant decreased the measured droplet size with the decrease being statistically significant for $D_{V0.1}$ and $D_{V0.5}$ at the 400-ppm level.

Treatment 2 Analyses

There was more variance (fig. 2) in the effects of water hardness and spray adjuvant for Treatment 2 than for Treatment 1. The data in figure 2 are presented as paired data (with or without a spray adjuvant in the tank solution) for three droplet size parameters ($D_{V0.1}$, $D_{V0.5}$, and $D_{V0.9}$) by water hardness level. Generally, there was no appreciable

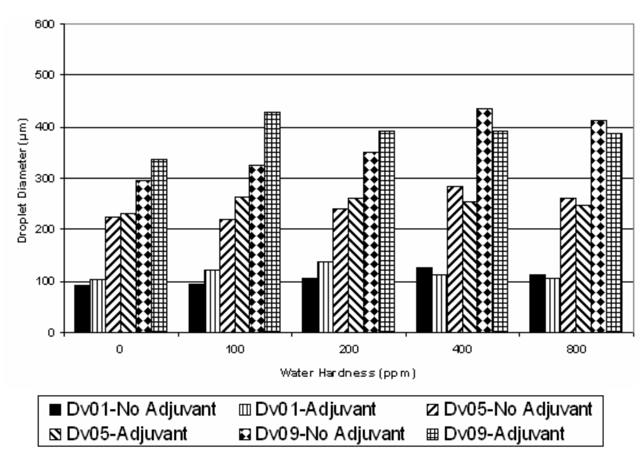

Figure 1. Effects of water hardness on $D_{V0.1}$, $D_{V0.5}$, and $D_{V0.9}$ with and without adjuvant added to the tank mix for a CP11TT 8008 Nozzle in a 56 m/s (125 mph) airstream orientated 45° in the airstream with a spray pressure of 207 kPa (30 psi).

Table 3. Statistical analyses of the effects of water hardness on droplet size parameters with and without adjuvant added to the tank mix for Treatment 1: CP11TT 8008 Nozzle in a 60 m/s (125 mph) airstream orientated 45° in the airstream with a spray pressure of 207 kPa (30 psi).

HARDNESS (ppm)	ADJU-VANT[a]	$D_{V0.1}$[b] (μm)	$D_{V0.5}$[b] (μm)	$D_{V0.9}$[b] (μm)	Relative Span	%Vol <100μm
0	N	91.9a	225.2a	295.3a	0.90a	11.6a
	Y	104.1a	231.7a	339.2a	1.01a	9.2a
100	N	94.1a	220.1a	324.7a	1.05a	11.4a
	Y	122.8b	264.9b	429.0b	1.16b	6.2b
200	N	105.5a	240.4a	351.1a	1.02a	9.1a
	Y	136.7a	261.9a	393.0a	0.98a	4.4a
400	N	126.7a	284.9a	434.9a	1.08a	5.9a
	Y	112.4b	253.0b	390.8b	1.10a	7.9a
800	N	112.9a	261.4a	411.5a	1.14a	7.9a
	Y	106.2a	247.1a	387.7a	1.14a	8.9a

[a] N = no adjuvant was added to tank solution, while Y = an adjuvant was added to tank solution.
[b] Within columns and by water hardness level, means followed by the same letter are not significantly different by Duncan's new multiple range test (P < 0.05).

change in droplet size as a result of different water hardness levels (fig. 2).

At 0-ppm water hardness, the addition of the spray adjuvant significantly lowered the $D_{V0.5}$ and $D_{V0.9}$ measurements (table 4) as compared to the droplet sizes from the tank solution with no adjuvant. For water hardnesslevels between 100 and 400 ppm, the addition of the spray adjuvant significantly increased the $D_{V0.1}$ and $D_{V0.5}$ measurements and numerical increases in the $D_{V0.9}$ measurement. There were no significant differences in the droplet size parameters at 800 ppm between the tank solutions with or without a spray adjuvant.

Relative Span and Percent Spray Volume Less than 100 μm

Relative span (RS) and the percent spray volume contained in droplets less than 100 μm (%Vol < 100 μm) are

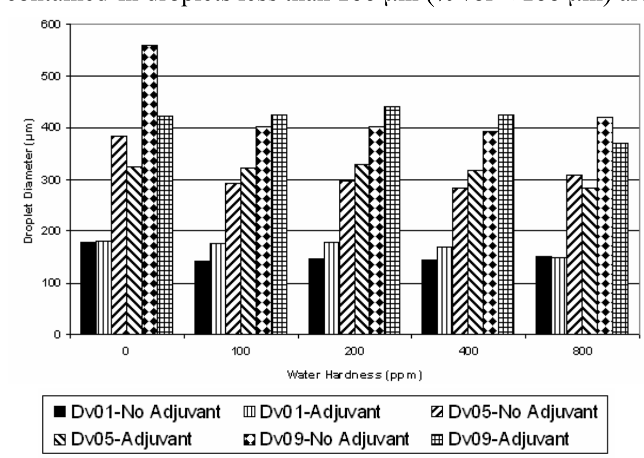

Figure 2. Effects of water hardness on $D_{V0.1}$, $D_{V0.5}$, and $D_{V0.9}$ with and without adjuvant added to the tank mix for a CP11TT 8008 nozzle in a 56 m/s (125 mph) airstream orientated 0° in the airstream with a spray pressure of 414 kPa (60 psi).

Table 4. Statistical analyses of the effects of water hardness on droplet size parameters with and without adjuvant added to the tank mix for Treatment 2: CP11TT 8008 Nozzle in a 60 m/s (125 mph) airstream orientated 0° in the airstream with a spray pressure of 414 kPa (60 psi).

Hardness	Adjuvant[a]	$D_{V0.1}$[b] (μm)	$D_{V0.5}$[b] (μm)	$D_{V0.9}$[b] (μm)	Relative Span	%Vol <100μm
0	N	178.6a	383.8a	559.7a	0.99a	2.6a
	Y	180.5a	324.8b	424.1b	0.75b	1.8b
100	N	142.0a	293.1a	403.8a	0.89a	4.6a
	Y	176.5b	323.8b	425.3b	0.77b	2.4b
200	N	146.5a	296.9a	403.0a	0.86a	4.2a
	Y	179.4b	328.9b	440.5a	0.79b	1.7b
400	N	143.1a	285.4a	393.8a	0.88a	4.0a
	Y	167.9b	318.7b	425.1b	0.81b	2.7b
800	N	151.4a	308.1a	419.5a	0.87a	3.6a
	Y	149.3a	284.3a	370.5a	0.78a	3.6a

[a] N = no adjuvant was added to tank solution, while Y = an adjuvant was added to tank solution.

[b] Within columns and by water hardness level, means followed by the same letter are not significantly different by Duncan's new multiple range test ($P < 0.05$).

often overlooked if only the $D_{V0.5}$ value is reported. RS is a reflection of how tight the droplet sizes are around the median value and can be thought of as the amount of control over the atomization process that an operator has for a particular combination of application conditions. The small mass associated with droplets that are less than 100 μm in diameter means that these droplet are very susceptible to drift, which is the displacement of the spray out of a target area by the prevailing wind.

The relative span was not significant for the adjuvant effect or the hardness/adjuvant interaction for Treatment 1 (table 2) but was significantly affected by water hardness, adjuvant, and the interaction of water hardness and spray adjuvant for Treatment 2. The %Vol < 100 μm was significantly affected by water hardness, adjuvant, and the interaction of water hardness and spray adjuvant for both treatments. For Treatment 1, the addition of spray adjuvant lowered the %Vol < 100 μm when water hardness varied from 0 to 200 ppm, but increased %Vol < 100 μm at the 400 and 800 ppm. The possible cause of this effect was discussed previously. For Treatment 2, the addition of the spray adjuvant significantly lowered the %Vol < 100 μm at all levels of water hardness except at 800 ppm.

Conclusions

- Water hardness levels from 0 to 800 ppm and/or the addition of a spray adjuvant to a spray solution had a significant effect on spray droplet size;
- The spray adjuvant, a non-ionic surfactant, increased most spray droplet size parameters and decreased the percent of spray volume contained in droplets less than 200 μm as long as the water hardness did not exceed 200 ppm.
- The spray adjuvant had little effect on relative span under high liquid shear sprays (Treatment 1) but lowered the relative span for sprays oriented 0° to the high speed airstream.
- Aerial applicators should test the water used in making tank solutions for water hardness before the addition of spray adjuvants. Applicator should be cautious with high levels of water hardness (i.e. > 200 ppm) as the drop size targeted by the equipment setup may be lower than that indicated by spray quality models and the addition of adjuvants to solutions with increased water hardness levels may reduce spray quality.

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